

## REMARKS

Claims 1-27 and 28-43 are pending in the Application. Claims 1-10 and 20-27 are allowed. Claims 11-19 and 28-43 stand finally rejected. Claim 28 is amended with this reply. Upon entry of the amendments, claims 1-27 and 28-43 remain pending.

Claim 28 has been rewritten to demonstrate manipulatively distinct steps recited in the method claim. The claim has the same scope and recites the same method as the previously unamended claim. No new matter is added and Applicants respectfully request entry of the amendments.

## OBVIOUSNESS TYPE DOUBLE PATENTING

Claim 35 is provisionally rejected for obviousness type double patenting in view of claims 1 and 7 of Co-pending Application 10/601,250<sup>1</sup>.

Claim 40 is provisionally rejected under obviousness type double patenting in view of claim 13 of Co-pending Application 10/623,922<sup>2</sup>.

Applicants maintain their position that the subject matter of the rejected claims is not obvious in light of the cited patents, for the reasons stated in earlier replies. However, in an effort to expedite prosecution, Applicants are filing Terminal Disclaimers to obviate both rejections. Accordingly, Applicants respectfully request the rejection be withdrawn.

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<sup>1</sup> Application Serial No. 10/601,250 corresponds to applicants docket 8540R-000002.

<sup>2</sup> Application Serial No. 10/623,922 corresponds to Applicants docket 8540R-000004.

## **DOUBLE PATENTING REJECTIONS UNDER 37 U.S.C. §101**

Claims 11, 15, 20, 28-32, and 43 are provisionally rejected under 35 U.S.C. § 101 as claiming the same invention as that of claims 1-7, 10, 35 and 37 of co-pending Application No. 10/601,250<sup>3</sup>. Applicants respectfully traverse the rejection and request reconsideration.

For statutory ( §101) double patenting rejections, a reliable test is whether a claim in the application could be literally infringed without literally infringing a corresponding claim in the patent. *In re Vogel*. The test is whether there is an embodiment of the invention that falls within the scope of one claim, but not the other. If, but only if, there is such an embodiment, then statutory double patenting would not exist. See generally MPEP § 804.II.A.

For convenience of reference, the rejected claims are shown in the left hand column of the following table, with the co-pending claims shown in the right hand column (Table A).

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<sup>3</sup> This is Applicants' Docket 8540R-000002.

TABLE A

<b>USSN 10/601,269 (H-203315; 8540R-000001) Claims 11, 15, 20, 28-32 and 43 Rejected under §101 for claiming the same invention as (10/601,250) 1-7, 10, 35, and 37</b>	<b>USSN 10/601,250 (GP-302786; 8540R-000002) Claims 1-7, 10, 35, and 37</b>
<p>11. (original) An automotive body panel comprising:</p> <ul style="list-style-type: none"> <li>a gel coat layer;</li> <li>a laminate layer; and</li> <li>a barrier coat disposed between the gel coat and the laminate layer,</li> </ul> <p>wherein the barrier coat comprises a polyester resin and reinforcing fibers of length 1 mm or less.</p> <p>15. (original) A body panel according to claim 11, wherein the laminate layer comprises a dicyclopentadiene resin and glass fibers of 6 mm in length or greater.</p> <p>20. (previously amended) A barrier coat composition comprising:</p> <ul style="list-style-type: none"> <li>a resin component comprising:</li> <li>80-100 parts of dicyclopentadiene resin and up to 20 parts of an isophthalic acid resin, and</li> <li>a reinforcing fiber component comprising fibers having a length of 1 mm or less mixed with the resin component.</li> </ul> <p>28. (previously amended) A method for preparing a composite article by spray up operation, comprising the steps of:</p> <ul style="list-style-type: none"> <li>applying a gel coat into a mold;</li> <li>applying a barrier coat over the gel coat in the mold; and</li> <li>applying a laminate formula over the barrier coat,</li> </ul> <p>wherein the laminate formula contains 20-60% by weight of first reinforcing fibers having a first length of 6 mm or greater and 40-80% by</p>	<p>1. A method for preparing a composite by spray up operation, comprising the steps of:</p> <ul style="list-style-type: none"> <li>applying a gel coat into a mold;</li> <li>applying a barrier coat over the gel coat; and</li> <li>applying a laminate formula over the barrier coat,</li> </ul> <p>wherein the laminate formula comprises 40-80% by weight paste and 20-60% by weight reinforcing fibers, wherein the paste comprises 70% or more by weight resin, up to 25% by weight filler, and an initiator composition;</p> <p>wherein the resin comprises an unsaturated polyester resin curable at a temperature of 50°C or lower; the filler comprises particles having a density lower than that of the resin, and the initiator composition contains an optional promoter or accelerator, the initiator composition being capable of initiating cure of the resin at a temperature of 50°C or lower.</p> <p>2. A method according to claim 1, wherein the gel coat is 0.2-2 mm thick, the barrier coat is 0.5-5 mm thick, and the laminate is 1-10 mm thick.</p> <p>3. A method according to claim 1, wherein the thickness of the composite is from 2-15 mm.</p> <p>4. A method according to claim 1, wherein the composite is an automobile body panel.</p> <p>5. A method according to claim 1, wherein the filler comprises glass hollow</p>

<p>weight of a paste comprising a laminate coat polyester resin;</p>	<p>microspheres.</p>
<p>wherein the barrier coat comprises second fibers having a length less than the first length dispersed in a barrier coat polyester resin.</p>	<p>6. A method according to claim 1, wherein the filler comprises polymeric hollow microspheres.</p>
<p>29. (previously amended) A method according to claim 28, wherein the gel coat applied to a thickness of 0.2 to 2 mm, the barrier coat is applied to a thickness of 0.5 to 5 mm, and the laminate layer is applied to a thickness of 1-10 mm.</p>	<p>7. A method according to claim 1, wherein the paste comprises 90% or more by weight resin and up to 5% by weight polymeric hollow microspheres.</p>
<p>30. (previously amended) A method according to claim 28, wherein the thickness of the composite article is from 2 to 15 mm.</p>	<p>10. A laminate composition comprising a paste and filler, wherein the paste comprises,</p>
<p>31. (previously amended) A method according to claim 28, wherein the composite article is an automotive body panel.</p>	<p>a dicyclopentadiene unsaturated polyester resin; polymeric hollow microspheres; and an initiator composition capable of initiating curing at a temperature of 50°C or less,</p>
<p>32. (previously amended) A method according to claim 28, wherein the laminate formula fiber comprises polymeric hollow microspheres.</p>	<p>and wherein the filler comprises reinforcing fibers having a length greater than or equal about 6 mm.</p>
<p>43. (previously amended) A method according to claim 35, comprising the steps of applying the gel coat to a thickness of 0.5-2 mm, applying the barrier coat to a thickness of 1-3 mm, and applying the laminate coat to a thickness of 2-5 mm.</p>	<p>34. A method according to claim 30, wherein the laminate resin composition comprises 90% or more by weight polyester resin and up to 5% by weight polymeric hollow microspheres.</p>
	<p>35. A method according to claim 34, wherein the polyester comprises a dicyclopentadiene resin.</p> <p>36. An automobile body panel, comprising a cured multilayer composite article comprising:</p> <p>a gel coat layer; a laminate layer; and a barrier layer disposed between the gel coat layer and the laminate layer,</p> <p>wherein the laminate layer comprises reinforcing glass fibers in a matrix of a cured polyester resin, wherein the matrix comprises up to 5% by weight of polymeric hollow microspheres and the polyester resin comprises a dicyclopentadiene polyester resin.</p> <p>37. A body panel according to claim 36, wherein the glass fibers are greater than or equal to about 12 mm in length.</p>

From the claims on the left hand versus the right hand column, it is readily seen that many embodiments of the invention that fall within the claims of the left hand column would not infringe the claims in the right hand column, and vice versa.

For example, claim 11 is drawn to an automotive body panel. Such an automotive body panel would not infringe the method claim 1 in the right hand column.

As another example, many of the other claims in the right hand column recite a limitation that the barrier coat contains fibers of less than 1 mm in length. Such a limitation is found in none of the claims on the right hand side. For these and many other reasons, Applicants respectfully submit that the rejected claims do not claim the same invention as claims 1-7, 10, 35 and 37 of Serial 10/601,250. For this reason, Applicant respectfully requests that the statutory double patenting rejection under 35 U.S.C. § 101 of the claims be withdrawn.

Claims 11, 42, and 43 are provisionally rejected under 35 U.S.C. § 101 as claiming the same invention as that of claim 10-12, and 18 of Co-pending Application 10/623,922<sup>4</sup>. Applicants respectfully traverse the rejection and request reconsideration.

The following table compares 11, 42, and 43 of the current application with claims 10-12 and 18 of the co-pending application. As was the case above, it is readily seen upon comparing the claims in the left and right columns that they do not claim the same invention.

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<sup>4</sup> This Application Serial No. corresponds to Applicants Docket 8540R-000004.

TABLE B

<b>USSN 10/601,269 (8540R-000001) Claims 11, 42, and 43 Rejected as claiming the same invention as (10/623,922) Claims 10-12 and 18</b>	<b>USSN 10/623,922 (8540R-000004) Claims 10-12, and 18;</b>
<p>11. (original) An automotive body panel comprising:      a gel coat layer;      a laminate layer; and      a barrier coat disposed between the gel coat and the laminate layer,      wherein the barrier coat comprises a polyester resin and reinforcing fibers of length 1 mm or less.</p> <p>35. (previously amended) A method of producing an automotive body panel comprising the steps of:      applying a gel coat composition to mold surface;      applying a barrier coat composition to the gel coat in the mold;      applying a fiber reinforced laminate composition comprising fibers having a first length onto the barrier coat and the mold;      curing at 50°C. or less; and      removing the cured article from the mold,      wherein the barrier coat comprises polyester resin and glass fibers having a second length shorter than the first length.</p>	<p>8. (previously amended) A composite article comprising a gel coat layer, a laminate layer, and a barrier layer disposed between the gel coat and laminate, wherein the laminate layer comprises reinforcing fibers in a cured polyester resin and the gel coat comprises a cured polyester polyurethane acrylate resin, wherein the gel coat layer forms a surface of the article that maintains 60% or more of its gloss after exposure to 4500kJ/m<sup>2</sup> of ultraviolet radiation, and      wherein the barrier layer comprises fibers having a length of 1 mm or less.</p> <p>10. (original) An article according to claim 8, wherein the total thickness of the article is 2-12 mm.</p> <p>11. (original) An article according to claim 8, wherein the total thickness of the article is 3-8 mm, the thickness of the gel coat is 0.5-1.5 mm, the thickness of the barrier coat is 0.75-2 mm, and the thickness of the laminate layer is 1-5 mm.</p> <p>12. (original) An article according to claim 8, wherein the reinforcing fibers comprise glass fibers having a length of 6 mm or greater.</p>

<p>42. (previously amended) A method according to claim 35, wherein the barrier coat comprises glass fibers having a length of 0.5 mm or less.</p> <p>43. (previously amended) A method according to claim 35, comprising the steps of applying the gel coat to a thickness of 0.5-2 mm, applying the barrier coat to a thickness of 1-3 mm, and applying the laminate coat to a thickness of 2-5 mm.</p>	<p>18. (previously amended) An automobile body panel, comprising a cured multilayer composite article comprising:</p> <ul style="list-style-type: none"> <li>a gel coat layer;</li> <li>a laminate layer; and</li> <li>a barrier layer disposed between the gel coat layer and the laminate layer,</li> </ul> <p>wherein the laminate layer comprises reinforcing glass fibers in a matrix of a cured polyester resin, and</p> <p>wherein the gel coat forms a surface of the body panel that maintains 60% or more of its gloss after exposure to 4500 kJ/m<sup>2</sup> of ultraviolet radiation, and</p> <p>wherein the barrier layer comprises fibers having a length of 1 mm or less.</p>
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For example, the claims of the right hand column all recite that the gel coat forms a surface body panel that maintains 60% or more of its gloss after UV exposure. Such a limitation is completely missing from the claims in the left hand column. As a consequence, it is possible for embodiments to exist that would infringe the left hand column of claims without infringing the right hand column claims.

To further illustrate, an automotive body panel having a gel cot layer that does not maintain 60% gloss after UV radiation, but which contains reinforcing fibers less than 1 mm long in its barrier coat would infringe claim 1 in the left hand column, but would not infringe claim 18 in the right hand column.

As demonstrated in the two Tables above, the cited claims do not claim the same invention. A rejection for statutory double patenting is improper, because the claims do not claim the same invention. To the extent the Examiner maintains a position the claims are obvious variants, Applicants note that they have mooted any such rejection by the filing of the enclosed Terminal Disclaimers.

**REJECTION UNDER 35 U.S.C. § 102**

Claims 28-34 are rejected under 35 U.S.C. § 102(b) as being anticipated by the Okayama reference (JP 2001-150559). The Examiner maintains his position that the structural limitations of the method steps are to be given no patentable weight under the authority of *Ex parte Pfeiffer*. Applicant respectfully submits that *Ex parte Pfeiffer* is inapplicable to the claims as amended. Accordingly, Applicants respectfully traverse the rejection and request reconsideration.

Applicants maintain their position that the method claims are patentable over the Okayama reference because the Okayama reference does not teach the compositions of the layers as they are laid down to form the composite article. The rule of *Pfeiffer* does not apply in this case. As developed in earlier replies, the method claims recite steps that are manipulatively distinct from the prior art.

To clarify this latter point and expedite prosecution, Applicants have rewritten claim 28 to be of the same scope as the earlier unamended claim. However, it is now even clearer that the recited steps are manipulatively distinct. Specifically, the claim now recites that applying the respective layers of the composite article involves providing specific compositions. Providing a specific composition is manipulatively

distinct from providing other compositions as suggested in the prior art. Because the claimed steps are manipulatively distinct, *Ex parte Pfeiffer* does not apply. Accordingly, the structural limitations are to be given patentable weight and the claims are patentable.

For this reason, and the others discussed in earlier replies, Applicants respectfully request the rejection be withdrawn.

#### **REJECTION UNDER 35 U.S.C. § 103**

Claims 35-43 are rejected under 35 U.S.C. § 103(a) as being unpatentable over the Okayama reference in view of the GB Patent (GB 1 493 547). Applicants respectfully traverse the rejection and request reconsideration.

The deficiencies of the Okayama reference are described above. Applicants respectfully submit the GB patent does not make up for those deficiencies. For example, *Ex parte Pfeiffer* is inapt for the same reasons as applied to the previous method claims. The method claims are thus patentably distinct over the Okayama reference and nothing in the GB Patent makes up for the deficiencies. Accordingly, Applicants respectfully request the rejection be withdrawn.

Claims 11, 15, 19, stand rejected under 35 U.S.C. § 103(a) as obvious in light of the GB Patent 1 493 547 alone. Applicants respectfully traverse the rejection and request reconsideration.

The Applicants respectfully maintain their position that the GB Patent does not teach the limitations of the rejected claims. The Office Action cites a number of passages in the GB patent that allegedly disclose a "laminate comprising a gel coat

layer, a laminate layer and a barrier layer disposed therebetween." Attached is a copy of the GB patent with the noted passages marked. Applicants wish to retract their statement that the GB Patent contained no teaching of a gel coat. However, Applicants maintain their position that the GB Patent has no disclosure of a barrier coat disposed between the gel layer and a laminate, as recited in the claims. See for example, the cited passages in the marked up version of GB '547 attached. Applicants do not see therein a disclosure of a barrier layer as recited in the claims. Nor does Applicant see a disclosure at page 3 lines 75-80 of glass fibers in the claimed range (1 mm or less).

For the further reason that the reference provides no motivation to provide such a layer, Applicant respectfully submits that claims 11, 15, and 19 are patentable under 35 U.S.C. § 103 in light of the reference. Accordingly, Applicants respectfully request the rejection be withdrawn.

Claim 17 and 18 are rejected as obvious over the GB Patent as applied to claims 11, 15, and 19, and further in view of the Maker reference. Applicants respectfully submit that the Maker reference does not cure the deficiencies of the GB Patent described above. Accordingly, Applicants respectfully request the Rejection be withdrawn.

## CONCLUSION

For the reasons discussed above, Applicants believe the claims 11-19 and 28-43 as amended are patentable over the references. Applicants respectfully request entry of the Amendments After Final and consideration of the arguments given above. Applicants believe they have pointed out clear error in applying the references, and have amended claim 28 to clarify the issues. In light of this, consideration of the Amendments and arguments after final is appropriate.

Prompt and favorable reconsideration is urgently solicited. In the alternative, Applicants respectfully request an Advisory Notice advising whether the amendments and arguments can be considered at this time. The Examiner is invited to contact Applicants' representative at the telephone number below, if that would be helpful in resolving any issue.

Respectfully submitted,

Dated: Feb 28 2006

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**1 493 547**

# PATENT SPECIFICATION

(11) **1 493 547**

- (21) Application No. 20364/76 (22) Filed 18 May 1976  
(31) Convention Application No. 584608  
(32) Filed 6 June 1975 in  
(33) United States of America (US)  
(44) Complete Specification published 30 Nov. 1977  
(51) INT CL<sup>2</sup> C08J 9/10  
(52) Index at acceptance

C3C 100 101 106 112 152 164 181 183 184 358 413 414 452 503  
520 570  
D1R 3A1 3A2M3 3A2MY 3A2X 3B4 3C1B 3C1Y 3D1A1  
3D1A2B 3D1A3A 3D1AY 3D2A 3D3C



## (54) LIGHTWEIGHT GLASS FIBRE REINFORCED POLYESTER ARTICLE AND METHOD OF MAKING THE SAME

(71) We, FREEMAN CHEMICAL CORPORATION, a corporation organised under the laws of the State of Delaware, U.S.A., with principal offices at 222 East Main Street, Port Washington, Wisconsin 53074, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

The invention concerns glass fibre articles utilizing unsaturated polyester resin syrup. Unsaturated polyester resin syrup and chopped glass fibres have been combined to produce glass fibre reinforced plastic articles. See "Polyesters and Their Applications", Bjorksten et al, Reinhold Publishing Corporation, 1956. The resulting articles have a high strength-to-weight ratio, good resiliency, electrical properties, resistance to corrosion, moldability. Such materials have been employed in aircraft components, boats, automobile components, light transmissive building sheeting, snowmobiles, golf carts, chairs, piping, tanks, window surrounds, bathroom vanities, bathtubs and shower stalls, building panels.

One type of product, known as a lay-up or spray-up article, is obtained by spraying the unsaturated polyester resin syrup along with appropriate free radical initiators, accelerators, surfactants, inhibitors, pigments, dyes or fillers against a stream of chopped glass fibres whereby the fibres are wetted and collected on a substrate. Customarily the wetted glass fibres are thereupon rolled or tamped to embed the loose ends of the glass fibres and eliminate gas pockets. The wetted fibres are retained in engagement with the substrate until the resinous components cure. Customarily the free radical initiator and the promoter are selected so that the curing will commence at room temperatures.

The curing is exothermic and causes a general increase in the temperature of the article. Complete cures in spray-up or lay-up operations normally require about one to four hours before the glass fibre reinforced article can be separated from the substrate and withdrawn as a product.

It is an object of the present invention to provide glass fibre reinforced unsaturated polyester resin articles which are without significant sacrifice in the strength of the product as compared with known articles but which will have a substantially lowered density which permits production of useful articles with less materials.

According to the present invention there is provided an article reinforced with chopped glass fibre containing 15 to 50% by weight of randomly oriented glass fibres confined in a continuous mass of cellular polymerised unsaturated polyester resin syrup containing 75 to 55% by weight of unsaturated polyester and 25 to 45% by weight of monomer, the cells of said mass containing a gas having a greater nitrogen content than the atmosphere, said article having a density of 15 to 60 pounds per cubic foot.

According to a further feature of the present invention there is provided a method of producing an article reinforced with chopped glass fibre which comprises wetting a stream of chopped glass fibres with a mixture comprising an unsaturated polyester resin syrup containing 75 to 55% by weight of unsaturated polyester and 25 to 45% by weight of monomer, an alpha hydroxy azo blowing agent, a polymerisation initiator and a metal salt accelerator, said mixture containing 0.5 to 5.0 parts by weight of said blowing agent for each 100 parts by weight of said resin syrup, collecting said wetted glass fibres as a coating on a substrate and allowing said coating to polymerise to provide a glass fibre reinforced article having

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- a density less than 75% of the density of a corresponding article which would be obtained in the absence of said blowing agent.
- In one method according to the invention, the mixture for wetting the glass fibres is formed by delivery to a mixing zone of a first stream containing the liquid resin syrup, and a second stream containing the blowing agent, mixing the two streams in the mixing zone and immediately spraying the resulting mixture onto a stream of chopped glass fibres.
- In one alternative method there is first formed a spray containing resin syrup and a second spray containing blowing agent, one spray being impinged on the other to form a combined spray, said combined spray being directed against a descending stream of chopped glass fibres.
- The wetting mixture for the glass fibres will in general include also surfactants, polymerisation inhibitors and fillers.
- Cellular plastic materials have been defined as "a plastic, the apparent density of which is decreased substantially by the presence of numerous cells disposed throughout its mass". The foaming of the present process arises from the nitrogen gas which is developed from the alpha hydroxy azo blowing agent. The expanding nitrogen gas creates the cells and is confined therein in concentrations which exceed the atmospheric nitrogen concentration.
- In contrast with polyurethane foams the polyester foams of the present invention are essentially free of urethane linkages and allophanate linkages.
- Figure 1 is a schematic illustration of apparatus useful in practicing a preferred embodiment of the present invention.
- Figure 2 is a fragmentary schematic illustration of equipment for practicing an alternative embodiment of the present invention.
- The three essential ingredients of the present invention are chopped glass fibres, unsaturated polyester resin syrups and alpha hydroxy azo blowing agents.
- #### Unsaturated Polyester Resin Syrup
- The unsaturated polyester resin syrup is a solution of an unsaturated polyester resin in a copolymerizable monomer which is usually styrene but may be other ethylenically unsaturated monomers such as vinyl toluene, divinyl benzene, acrylic acid, methacrylic acid, alkyl acrylates and meth acrylates, ortho - chlorostyrene, alpha - methylstyrene, ethylene glycol dimethacrylate. The unsaturated polyester resin is formed by polyesterification of polyol and polycarboxylic acid or polycarboxylic acid anhydride at least a portion of which contains ethylenic unsaturation.
- Typical polyols include glycols such as ethylene glycol, propylene glycol, butylene glycol, neopentyl glycol, diethylene glycol, di-propylene glycol, polyethylene glycol, polypropylene glycol and the like. The polycarboxylic acid or anhydride may include materials which do not possess ethylenic unsaturation such as phthalic acid, phthalic anhydride, isophthalic acid, terephthalic acid, adipic acid, succinic acid, glutaric acid, malonic acid, pimelic acid, sorbic acid, halogenated dibasic acids. Typical unsaturated dicarboxylic acids or anhydrides include maleic acid, maleic anhydride, fumaric acid, endomethylene - tetrahydrophthalic acid or anhydride, itaconic acid and the like. Typically the unsaturated polyester resin is prepared by polyesterification of an excess of polyol with polycarboxylic acid. Typically at least 40 mol percent of the polycarboxylic acid is ethylenically unsaturated polycarboxylic acid. The acid and polyol are cooked in the presence of a polyesterification catalyst until the polyesterification is essentially completed as indicated by the acid number of the resulting product being reduced to 30 or less. The unsaturated polyester resin syrup contains about 1 part by weight of copolymerizable monomer for every 1 to 10 parts by weight of the unsaturated polyester resin.
- As stated the unsaturated polyester resin syrup contains 25 to 45 weight percent monomer and 75 to 55 weight per cent unsaturated polyester. In connection with the present invention, when the monomer content is below about 25 percent, the resulting syrup is difficult to spray. When the monomer content exceeds 45 weight percent the monomer tends to separate out as a distinct phase from the foaming, ungelled resin.
- #### Polymerisation Initiator
- Preferably the polymerisation initiator employed is a high temperature initiator and suitably provided from in an amount of from 0.2 to 2 percent by weight of the unsaturated polyester resin syrup. Useful initiators include tertiary butyl perbenzoate ditertiary butyl perbenzoate, cumene hydroperoxide, methylethylketone peroxide and tertiary butyl hydroperoxide. These initiators are ineffective at room temperature but become effective when the temperature is increased, particularly in the presence of metal salt promoters.
- The polymerisation initiator is preferably incorporated in the unsaturated polyester resin syrup. Peroxy type initiators, if employed, are used in the unsaturated polyester resin syrup. Other types of initiators may be combined with the alpha hydroxy azo blowing agent or with the unsaturated polyester resin syrup.
- #### Metal Salt Accelerators, i.e. Promoters
- The present compositions contain metal

5 salt accelerators preferably in amounts from 1 to 100 parts by weight per million (p.p.m.) of the weight of the unsaturated polyester resin syrup. A preferred promoter is copper naphthenate solution although cobalt salts, vanadium salts, manganese salts, calcium salts, magnesium salts can also be employed.

#### Surfactants

10 If it is desired to produce a foamed product having relatively uniform foam cell sizes, a small quantity of a silicone surfactant is employed in the amount of 0.1 to 2.5 weight percent of the unsaturated polyester resin syrup.

#### Inhibitors

15 Customarily unsaturated polyester resin syrups are provided with polymerization inhibitors to forestall unintended premature gelation.

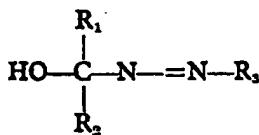
#### Fillers

20 The unsaturated polyester resin syrup may be filled with inert materials such as pigments, dyes, aluminum oxide trihydrate, silica, limestone, ground glass, clays, mica and thixotropic additives such as silica aerogel.

25 Where thixotropic additives are employed they are used in quantities ranging from about 1/2 to about 3 percent by weight of the unsaturated polyester resin syrup. The other inert fillers may be employed up to about an equal weight of the unsaturated polyester resin syrup.

30 A particularly preferred inorganic filler is powdered aluminum oxide trihydrate from about 70 to 110 percent of the weight of the unsaturated polyester resin syrup. At concentrations above about 110 percent by weight aluminum oxide trihydrate, the resulting mixture cannot be sprayed. At concentrations below about 70 percent by weight aluminum oxide trihydrate, no substantial benefit is observed. However when the aluminum oxide trihydrate is employed from about 70 to 110 percent by weight of the unsaturated polyester resin syrup, the resulting article exhibits outstanding flame spread ratings and smoke index ratings.

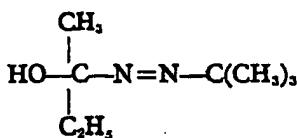
35 The Alpha Hydroxy Azo Blowing Agent  
40 Suitable alpha hydroxy azo blowing agents have the following general formula:



45 wherein  $R_1$  and  $R_2$  are lower alkyl groups having from 1 to 4 carbon atoms and  $R_3$  is a tertiary alkyl group having 4 to 8

50 carbon atoms or an aromatic substituted tertiary alkyl group having 9 to 12 carbon atoms. Examples of  $R_3$  substituent are the tertiary-butyl radical and the alpha-cumyl radical.

55 A preferred alpha hydroxy azo blowing agent is identified as blowing agent I having the following formula:



60 The azo blowing agent may be employed full strength or it may be diluted with inert solvents which will not impede the polymerization of the polyester resin syrup. Such solvents include mineral oil and styrene for example.

#### Glass Fibres

65 The glass fibres employed in the present reinforced articles are normally the type which are conventionally used in glass fibre reinforced articles, that is, chopped glass, roving with an average length of about 3/8 inch to about 4 inches although lengths ranging from 1/2 inch to 1 inch are normally preferred. Commercial glass roving is usually coated with a silane sizing to improve bond with the resins. The glass fibres normally constitute from about 5 to 30 weight percent of the product.

#### The Present Process

70 As shown in Figure 1, a tank 10 is supplied with an unsaturated polyester resin syrup containing suitable quantities of free radical initiator, promoter, surfactant, and, if desired, inert fillers. A tank 11 contains the alpha hydroxy azo blowing agent in liquid form.

75 A spool 12 contains glass fibre rovings of the type customarily employed in producing glass fibre reinforced plastic articles.

80 Unsaturated polyester resin syrup from the tank 10 is delivered through a tube 13 to a spray gun 14. The alpha hydroxy azo blowing agent is delivered from the tank 11 through a tube 15 to the spray gun 14. A supply of pressurized air is delivered through the tube 16 to the spray gun 14. Within the spray gun 14 there is a mixing chamber where the unsaturated polyester resin syrup and the alpha hydroxy azo blowing agent are mixed and formed into a spray 17 by the atomization from the compressed air in the spray gun 14.

85 Concurrently the glass fibre roving 18 is drawn from the spool 12 and chopped in a chopper 19 to form a descending cloud 20 of chopped glass fibres which impinge the spray 17 and thereby become wetted with

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the spray mixture. The wetted fibres 17 fall onto a substrate 21 and are collected as a coating 22. The exposed surface 23 of the substrate 21 is coated with a suitable mold release agent to facilitate subsequent separation of the coating 22 from the substrate 21. Alternatively the substrate 21 may be a final product which will contain the coating 22 in its completed form. An example is where the substrate 21 is a premolded sheet of acrylic resin shaped into the form of a bathtub. The coating 22, as deposited, contains randomly oriented glass fibres and objectionable air pockets. Accordingly, it is preferred that the coating 22 be rolled and/or tamped to embed any projecting glass fibres and to minimize the unintended porosity resulting from unwanted air pockets. The rolling and tamping should be carried out promptly inasmuch as the mixture of unsaturated polyester resin syrup and alpha hydroxy azo blowing agent commences gelation almost immediately upon mixing. The coating 22, following rolling and/or tamping, should be allowed to remain quiescent for a suitable time to allow the coating to develop an exotherm, to complete cure and commence cooling.

#### Example 1

A commercially available unsaturated polyester resin is fabricated from 105 mol parts by weight propylene glycol, 50 mol parts isophthalic acid and 50 mol parts by weight maleic anhydride. The three ingredients are cooked to a final acid value between 17 and 25, measured at 60 percent by weight solids content in methyl 'Cellosolve' [Cellosolve is a Registered Trade Mark] solvent. 73 parts by weight of the described unsaturated polyester resin is combined with 27 parts by weight of styrene to produce an unsaturated polyester resin syrup having an acid value of 27 to 33.

The unsaturated polyester resin syrup was combined with 0.5 weight percent tertiary butyl perbenzoate as a free radical initiator, 1 percent by weight silicone fluid as a surfactant, 4-1/2 parts per million by weight of copper naphthenate as an accelerator. No filler was employed in this example. The chopped glass roving was a type known in the trade as 60-end roving chopped into lengths of 1-1/2 to 3 inches.

The alpha hydroxy azo blowing agent I was employed at a flow rate of 1 percent by weight of the unsaturated polyester resin flow rate. Both the unsaturated polyester resin and the alpha hydroxy azo blowing agent I were introduced into a spray gun combined with a glass roving chopper. The chopped glass fibres, wetted with the combined spray, were applied against a drum lid mould which was previously coated with a mould release agent. The spray was applied in three passes

over the surface. The coated drum lid was rolled with a glass compacter roller and allowed to rise freely at room temperature. The article was demolded from the drum lid after about 15 minutes. The article had a flexural strength of 4100 psi, a flexural modulus of  $0.26 \times 10^6$  psi, a tensile strength of 2900 psi, a tensile modulus of  $0.217 \times 10^6$  psi, a density of 26 pounds per cubic foot and a closed cell content of about 92 percent. The article contained 26 percent by weight glass fibres. The starting thickness of the article after compacter rolling was 0.125 inch. After curing the final article thickness was 0.432 inch.

#### Example 2

For purposes of comparison conventional article was prepared from the unsaturated polyester resin syrup described in Example 1 combined with an equal weight of powdered aluminum oxide trihydrate. The 50-50 mixture of aluminum oxide trihydrate and unsaturated polyester resin syrup was sprayed with chopped glass fibres to produce an article having a final density after cure of about 90 pounds per cubic foot.

#### Example 3

The filled unsaturated polyester resin syrup of Example 2 including an equal weight of aluminum oxide trihydrate was combined in a spray gun as described in Example 1 with 1 percent by weight of alpha hydroxy azo blowing agent type I. Chopped glass fibres wetted with the combined spray produced an article having a density of about 45 pounds per cubic foot. This article was subjected to combustion tests in an Underwriters' Laboratories test and yielded a smoke index of 182 and a flame spread of 44. The glass content in the panel was 20 percent by weight. The panel had a thickness from about 1/4 inch to about 1/2 inch.

The article of Example 3 had a density (45 p.c.f.) about 50 percent of the density of the Example 2 article (90 p.c.f.).

#### Example 4

The foamed resinous materials in accordance with the present invention were employed in the construction of a number of boats, one of which will be described. A 21 foot long inboard motor boat hull was prepared from a commercial hull mould which itself was fabricated from reinforced polyester materials. Initially a mould release agent was applied to the surface of the hull mould by wiping with a rag. Thereafter a pigmented gel coat was sprayed over the entire surface and allowed to cure. Thereafter a conventional unsaturated polyester resin and glass fibre spray-up coating was applied over the cured gel coat in an average thickness of about 80 mils. This spray-up

coating was allowed to cure. Thereafter a number of pre-cut wooden reinforcing stringers and cross-pieces were applied against the cured spray-up coating by press fitting.

Thereafter a polyester resin foam and glass fibre coating of this invention was applied to the original spray-up coating to an initial thickness of about 15 mils prior to foaming. After foaming the coating had a thickness of about 40 mils. The foam-glass fibre coating covered the side surfaces of the wooden stringers and cross-pieces and served as a binder for retaining them permanently in position.

After the foamed resin coating had been cured, a further skin coating of unsaturated polyester resin and glass fibres was applied as a spray-up coating in a thickness of about 80 mils. The total thickness of the boat hull was 0.4 to 0.5 inch. The total weight of the boat hull including wooden stringers and cross-pieces was about 400 pounds.

Corresponding boats are made commercially from conventional polyester resin and glass spray-up techniques in two separate spray-up operations having a total thickness of 0.25 to 0.375 inch. A conventional boat hull, if overturned, will sink in water. The boat hull manufactured in accordance with this invention had the same total weight as the conventional boat hull but floated when overturned.

The foamed polyester glass spray-up employed a polyester fabricated from a 50/50 weight percent mixture of isophthalic acid and maleic anhydride esterified with a slight excess of propylene glycol to an acid value of about 18 at 60 percent solids. The polyester is mixed into a syrup containing 40 percent by weight styrene, 0.5 weight percent of a silicone surfactant, 0.7 weight percent tertiary butyl perbenzoate and 6 parts by weight per million of copper naphthenate. This material is combined with 1.75 weight percent (based on the weight of the polyester syrup) of the azo blowing agent I. The chopped glass fibres constitute 18 percent of the weight of the foam layer. Two samples of the foamed glass layer taken at different times showed densities of 23 pounds per cubic foot and 34 pounds per cubic foot.

The foamed polyester-glass fibre coating served to adhere the wooden stringers and wooden cross-pieces firmly to the boat hull surfaces.

#### General

Inhibitors which are customarily employed with unsaturated polyester syrups are not effective in the presence of alpha hydroxy azo blowing agents. In a typical unsaturated polyester resin syrup, the addition of 1,000 p.p.m. hydroquinone will extend the gel time

about three-fold. Where an alpha hydroxy azo blowing agent is employed, 1,000 p.p.m. hydroquinone extends the gel time by only about 10 percent.

#### Alternative Method

Referring to Figure 2, an alternative method for making the present spray-up, lay-up articles is illustrated which employs two different spray nozzles identified by the numerals 24, 25. Compressed air from a tube 16A is delivered to both of the nozzles 24, 25. The unsaturated polyester resin syrup is delivered from 10 through a tube 13A to the nozzle 24. The alpha hydroxy azo blowing agent is delivered from 11 through a tube 15A to the spray nozzle 25 whence it emanates as a spray 26. The unsaturated polyester resin syrup is delivered as a spray 27 from the nozzle 24. The two sprays 26, 27 combine to produce a composite spray 28 wherein the alpha hydroxy azo blowing agent is intimately admixed with the unsaturated polyester resin syrup. The combined spray 28 wets a descending cloud 20A of glass fibres to form a coating 22A on the substrate 21A.

Some of the useful products which can be fabricated from the present process include one-piece tub and shower stall units, bathroom vanities, automobile fenders and hoods, cold molded formed shapes such as building window surrounds and cornices, backing for thermoformed acrylic sheeting, snowmobile shrouds, barge covers, building infill panels, mobile homes, liners for railroad boxcars, tote boxes, silo roofs and panels, tanks and the like, boat hulls, surfboards.

#### WHAT WE CLAIM IS:—

1. An article reinforced with chopped glass fibre containing 15 to 50% by weight of randomly oriented glass fibres confined in a continuous mass of cellular polymerised unsaturated polyester resin syrup containing 75 to 55% by weight of unsaturated polyester and 25 to 45% by weight of monomer, the cells of said mass containing a gas having a greater nitrogen content than the atmosphere, said article having a density of 15 to 60 pounds per cubic foot.

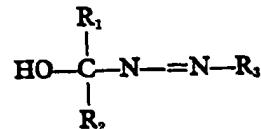
2. An article reinforced with chopped glass fibre according to claim 1 wherein the cellular mass contains 70 to 110% by weight of powdered aluminium oxide trihydrate based upon the weight of said polymerised unsaturated polyester resin in the article.

3. An article reinforced with chopped glass fibre according to claim 1 substantially as herein described.

4. A method of producing an article reinforced with chopped glass fibre as claimed in claim 1 which comprises wetting a stream

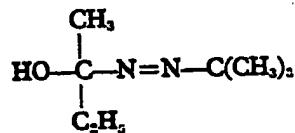
- of chopped glass fibres with a mixture comprising an unsaturated polyester resin syrup containing 75 to 55% by weight of unsaturated polyester and 25 to 45% by weight of monomer, an alpha hydroxy azo blowing agent, a polymerisation initiator and a metal salt accelerator, said mixture containing 0.5 to 5.0 parts by weight of said blowing agent for each 100 parts by weight of said resin syrup, collecting said wetted glass fibres as a coating on a substrate and allowing said coating to polymerise to provide a glass fibre reinforced article having a density less than 75% of the density of a corresponding article which would be obtained in the absence of said blowing agent.
5. A method according to claim 4, wherein in the mixture for wetting the glass fibres is formed by delivery to a mixing zone of a first stream containing the liquid resin syrup and a second stream containing the blowing agent, mixing the two streams in the mixing zone and immediately spraying the resulting mixture onto a stream of chopped glass fibres.
10. A method according to claim 4, wherein there is formed a first spray containing resin syrup and a second spray containing blowing agent, one spray being impinged on the other to form a combined spray, said combined spray being directed against a descending stream of chopped glass fibres.
15. A method according to claim 4, wherein the resin syrup includes powdered aluminium oxide trihydrate in an amount sufficient to constitute 70 to 110% by weight of the said resin syrup.
20. A method according to any of claims 4 to 6, wherein the resin syrup includes powdered aluminium oxide trihydrate in an amount sufficient to constitute 70 to 110% by weight of the said resin syrup.
25. A method according to any of claims 4 to 6, wherein the resin syrup includes powdered aluminium oxide trihydrate in an amount sufficient to constitute 70 to 110% by weight of the said resin syrup.
30. A method according to any of claims 4 to 6, wherein the resin syrup includes powdered aluminium oxide trihydrate in an amount sufficient to constitute 70 to 110% by weight of the said resin syrup.
35. A method according to any of claims 4 to 6, wherein the resin syrup includes powdered aluminium oxide trihydrate in an amount sufficient to constitute 70 to 110% by weight of the said resin syrup.

to 7, wherein the alpha hydroxy azo blowing agent has the formula



wherein  $R_1$  and  $R_2$  are lower alkyl groups having from 1 to 4 carbon atoms and  $R_1$  is a tertiary alkyl group having from 4 to 8 carbon atoms or an aromatic substituted tertiary alkyl group having from 9 to 12 carbon atoms.

40. A method according to claim 8 wherein in the alpha hydroxy azo blowing agent has the formula



45. A method according to any of the preceding claims 4 to 9, wherein the collected wetted fibres are rolled or tamped to embed loose ends of the glass fibres and eliminate gas pockets.

50. A method of producing an article reinforced with chopped glass fibre according to claim 1, substantially as herein described.

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1403547 COMPLETE SPECIFICATION  
1 SHEET This drawing is a reproduction of  
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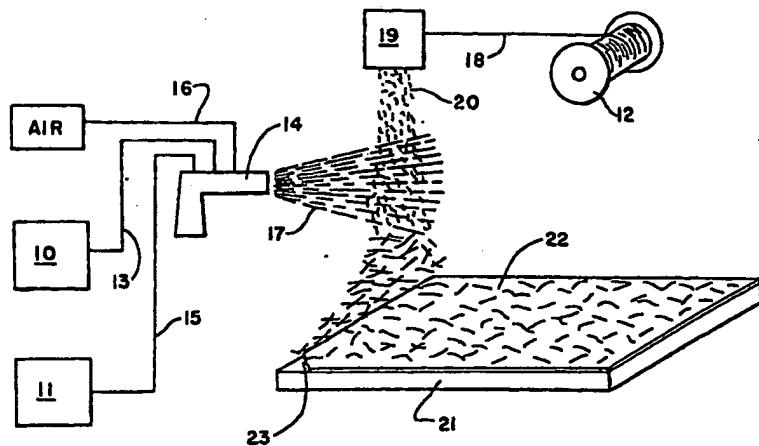


FIG. 1

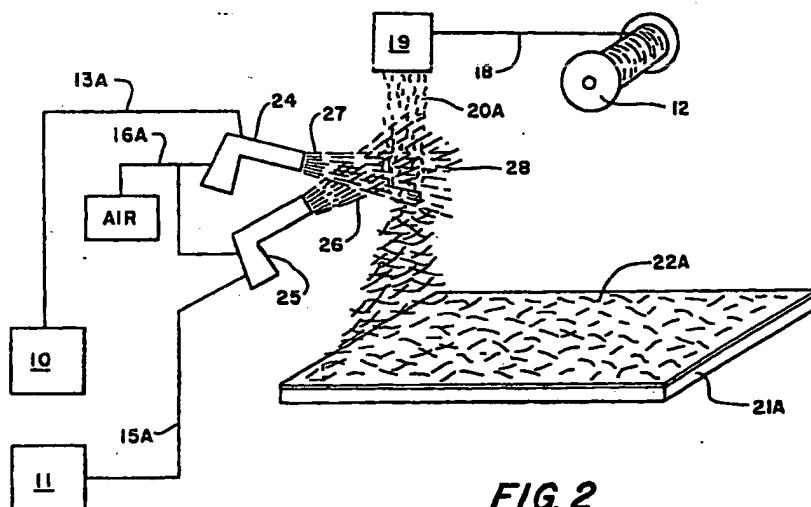


FIG. 2